

Erratum

Natural Resonance Theory. I. General Formalism

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The code for the natural resonance theory (NRT) program contains an error in the routine to calculate $D(\underline{W})$ (SR GETDW), the root-mean-square deviation of the reference weighted density matrix from the true density matrix,

$$D(\underline{W}) = \min_{\{\hat{W}^{(r)}\}} \left\| \hat{\Gamma} - \sum_r W^{(r)} \hat{\Gamma}^{(r)} \right\|,$$

where $\{\hat{\Gamma}^{(r)}\}$ denotes a set of reference structures with resonance weights $\{W^{(r)}\}$.

The updated code calculates $D(\underline{W})$ in accord with the description in the natural bond orbital (NBO) program manual and the original NRT article. The revision has been sent to commercial providers of the NBO algorithm. Users of the stand-alone NBO program should make the following changes:

Old: CALL MULTI(FW,A(I35),A(I33),
A(I18),IRESET,LNAO,NREF)

New: CALL MULTI(FW,A(I35),A(I33),
A(I18),IRESET,LNAO,NREF,NVAL),

Old: SUBROUTINE MULTI(FW,GAMMAW,WGT,
SCR,IRESET,LVAL,NREF)

New: SUBROUTINE MULTI(FW,GAMMAW,WGT,
SCR,IRESET,LVAL,NREF,NVAL),

Old: SUBROUTINE GETDW(DW,GAMMAW,WGT,
LVAL,NREF)

New: SUBROUTINE GETDW(DW,GAMMAW,WGT,
LVAL,NREF,NVAL),

and add the NVAL variable to the end of all CALL GETDW commands in subroutine MULTI.

In subroutine GETDW the following changes were made:

Old: DATA ZERO/0.0DO/

DW = ZERO
DO 20 IREF = 1,NREF
IF(WGT(IREF).GT.ZERO) THEN
DO 10 I = 1,LVAL
TMP = WGT(IREF)
* GAMMAW(I,IREF)
DW = DW + TMP * TMP
10 CONTINUE
END IF
20 CONTINUE
DW = SQRT(DW / LVAL)
RETURN
END

New: DATA ZERO,TWO/0.0DO,2.0DO/

IJ = 0
DW = ZERO
DO 30 J = 1,NVAL
DO 20 I = 1,J
IJ = IJ + 1
DW2 = ZERO

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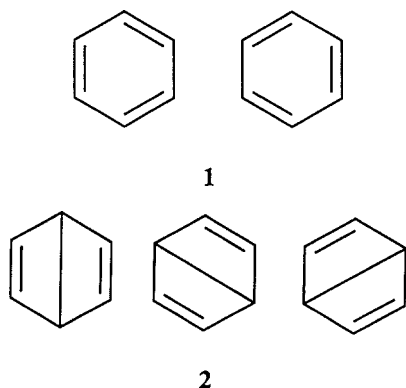
DO 10 IREF = 1,NREF
  IF(WGT(IREF).GT.ZERO) THEN
    TMP = WGT(IREF)
      * GAMMAW(IJ,IREF)
    DW2 = DW2 + TMP
  END IF
10 CONTINUE
  IF(I.NE.J) THEN
    DW = DW + TWO * DW2 * DW2
  ELSE
    DW = DW + DW2 * DW2
  END IF
20 CONTINUE
30 CONTINUE
DW = SQRT(DW / NVAL / NVAL)
RETURN
END

```

The error manifested itself through incorrect reference structure weightings, which then produced incorrect values of natural bond orders and other resonance weighted properties. We looked at a sampling of molecules to determine the effect of this correction, and some representative cases are described below.

Benzene

The two Kekulé, **1**, and three Dewar, **2**, resonance forms were specified as reference structure for benzene using the NRTSTR keyword.



The results for the old and new $D(W)$ routines are summarized in Table I. The new routine finds the Dewar structures to be weighted less than before, and there is a corresponding increase in C—C bond order of about 2%.

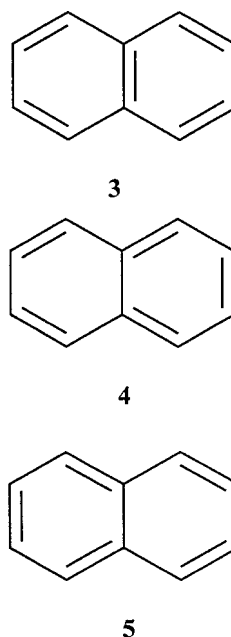
Naphthalene

For naphthalene only the three Kekulé structures, **3–5**, were used as NRTSTR defined reference struc-

TABLE I.
Summary of Results for New $D(W)$ Routine.

	Original Routine	Corrected Routine
Benzene		
Total Kekulé weight (%)	40.74	58.80
Total Dewar weight (%)	12.30	7.71
$D(W)$	0.01619	0.02092
Adjacent C—C bond order	1.4094	1.4431
Formamide		
Structure 6 (%)	62.66	63.70
Structure 7 (%)	30.40	29.11
$D(W)$	0.03329	0.03595
C—O bond order	1.7275	1.7412
C—N bond order	1.3122	1.3008
Boron trifluoride		
Structure 8 (%)	48.84	76.65
Structure 9 (%)	32.19	4.37
$D(W)$	0.02674	0.03495
B—F(2,4) bond order	1.0603	1.0604
B—F ₃ bond order	1.5278	1.8315
Average B—F bond order	1.216	1.317

tures. (The addition of the 42 singly, doubly, and triply excited Dewar-type structures did not change these results.)



The percentage weighting of the structures changed very little with the new routine. Structure **3** went from 28.62 to 29.05%, while structures **4** and **5** both went from 17.94 to 17.42%. The $D(W)$ increased

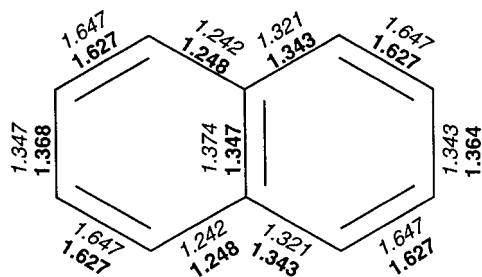
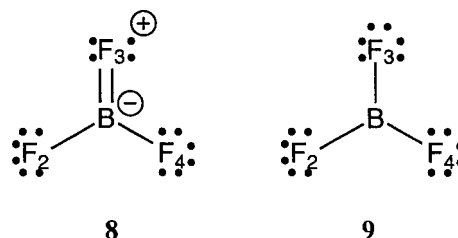


FIGURE 1. A comparison of NRT calculated bond orders with the old $D(W)$ routine (italics) and the new $D(W)$ routine (bold).

from 0.01612 to 0.01848. The bond order changes are shown in Figure 1. The largest percentage change in bond order between the two methods is 2%.

Boron Trifluoride

Boron trifluoride is an example of a severe disagreement between the old and new routines. Structures 8 and 9 were used as the NRTSTR reference structures, which forced an unsymmetrical description of the bonding.

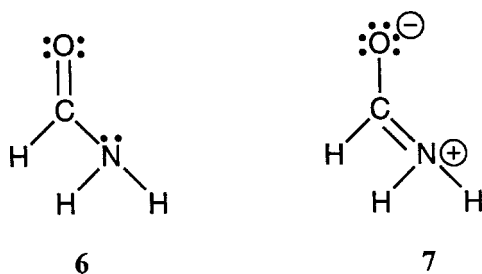


The results are shown in Table I. The old $D(W)$ routine used a large percentage of the covalent structure, 9, while the new $D(W)$ routine uses a negligible amount. The large change in B—F₃ bond order is offset somewhat by finding the average B—F bond order, but the error is still on the order of 10%.

In summary, we found and corrected an error in the NRT code that affects the reference structure weighting procedures. In most cases the differences between the incorrect and correct code result in small errors, usually on the order of 1–2%. In some cases, such as BF₃, the errors can be as large as 10%. The corrected code has been distributed to NBO software distributors, and the stand-alone NBO program can be fixed with the replacement of one small subroutine.

Formamide

Structures 6 and 7 were used as the NRTSTR reference structures.



The results are shown in Table I. The percent change in calculated bond order is less than 1%.